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A special kind of quasi-homogeneity occurring in thermodynamic potentials of standard thermodynamics is pointed out. Some formal consequences are also discussed.

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I. INTRODUCTION

Quasi-homogeneous functions have been introduced in the framework of standard thermodynamics with the aim to studying scaling and universality near the critical point [1,2]. A common synonymous of "quasi-homogeneous function" is "generalized homogeneous function" [see e.g. [1–3]]. We wish to point out here that quasi-homogeneity can be an useful tool in the framework of standard thermodynamics, when one considers intensive variables as independent variables for the equilibrium thermodynamics description of a system. In fact, homogeneity for the fundamental equation in the entropy representation [and in the energy representation] is well-defined in terms of the standard Euler theorem for homogeneous functions [4]. One simply defines the standard Euler operator (sometimes called also Liouville operator) and requires the entropy [energy] to be an homogeneous function of degree one. When the other thermodynamic potentials which are obtained from the entropy [energy] are taken into account by means of suitable Legendre transformations, then part of the independent variables are intensive [4]. The thermodynamic potentials are still homogeneous of degree one in the extensive independent variables, but a different rescaling is appropriate for the independent variables. For example, let us consider the Gibbs potential $G(T,p,N)$ for a system which is described by means of three independent variables T,p,N. G is homogeneous of degree one when the system is rescaled by λ, such a rescaling corresponding only to a rescaling $N \to \lambda N$, because T and p are intensive and remain unchanged under rescaling of the system. This is evident because, as it is well known, one has $G = \mu(p,T)N$, where μ is the chemical potential. Actually, one could also define G as a quasi-homogeneous function of degree one with weights $(0,0,1)$. Then the behavior under scaling is better defined. A mathematical treatment of the same problem is found in Ref. [5]. The approach we present here is characterized by the more general setting allowed by the technology of quasi-homogeneous functions; the sections on the Gibbs-Duhem equation and the on Pfaffian forms contain a further analysis of some formal aspects of standard thermodynamics.

II. QUASI-HOMOGENEOUS FUNCTIONS AND THERMODYNAMICS

Given a set of real coordinates $x^1,\dots,x^n$ and a set of weights $\boldsymbol{\alpha} \equiv (\alpha_1,\dots,\alpha_n) \in \mathbb{R}^n$, a function $F(x^1,\dots,x^n)$ is quasi-homogeneous of degree r and type $\boldsymbol{\alpha}$ [6] if, under dilatations by a scale factor $\lambda > 0$ one finds

$$F(\lambda^{\alpha_1}\, x^1,\dots,\lambda^{\alpha_1}\, x^n) = \lambda^r\, F(x^1,\dots,x^n). \tag{1}$$

A differentiable quasi-homogeneous function satisfies a generalized Euler identity:

$$D\, F = r\, F, \tag{2}$$

where D is the Euler vector field

$$D \equiv \alpha_1\, x^1\, \frac{\partial}{\partial x^1} + \dots + \alpha_n\, x^n\, \frac{\partial}{\partial x^n}. \tag{3}$$

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Notice that (2) is a necessary and sufficient condition for a differentiable function to be quasi-homogeneous [6]. It is also interesting to define quasi-homogeneous Pfaffain forms. A Pfaffian form

$$\omega = \sum_{i=1}^{n} \omega_i(x)\, dx^i \tag{4}$$

is quasi-homogeneous of degree $r \in \mathbb{R}$ if, under the scaling

$$x^1, \ldots, x^n \to \lambda^{\alpha_1}\, x^1, \ldots, \lambda^{\alpha_n}\, x^n \tag{5}$$

one finds

$$\omega \to \lambda^r\, \omega. \tag{6}$$

This happens if and only if the degree of quasi-homogeneity $\deg(\omega_i(x))$ of $\omega_i(x)$ is such that $\deg(\omega_i(x)) = r - \alpha_i \quad \forall i = 1, \ldots, n$. For a discussion about quasi-homogeneity and for further references, see [7].

A. quasi-homogeneous potentials in standard thermodynamics

Let us consider a thermodynamic potential $R(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n)$ depending on k intensive variables $y^1, \ldots, y^k$ and $n-k$ extensive variables $x^{k+1}, \ldots, x^n$. R is required to be quasi-homogeneous of degree 1 and its type is

$$\boldsymbol{\alpha} = (\underbrace{0, \ldots, 0}_{k}, \underbrace{1, \ldots, 1}_{n-k}). \tag{7}$$

Then, one has

$$R = \sum_{i=k+1}^{n} x^i\, \frac{\partial R}{\partial x^i}. \tag{8}$$

This expression of the thermodynamic potentials is well-known, it is sometimes referred to as the identity satisfied by the potentials at fixed intensive variables [8]. A treatment on a mathematical ground of the same topic is found in Ref. [5]. It is evident that, in order to ensure that R is a degree one quasi-homogeneous function, the intensive variables can be at most $n-1$, in which case (cf. also the following section)

$$R = x^n\, \frac{\partial R}{\partial x^n} \equiv x^n\, r(y^1, \ldots, y^{n-1}), \tag{9}$$

where $r(y^1, \ldots, y^{n-1})$ is of degree zero.
We recall that, given the fundamental equation of thermodynamics in the energy [entropy] representation, one can obtain other fundamental equations by means of the Legendre transform [4]. It is easy to show that:

the Legendre transform with respect to a variable of weight α of a quasi-homogeneous function of degree r is a quasi-homogeneous function of degree r with the weight α changed into the weight $r - \alpha$ of the Legendre-conjugate variable (theorem 2 of [1]).

Moreover,

the partial derivative with respect to a variable of weight α of a quasi-homogeneous function R of degree r is a quasi-homogeneous function of degree $r - \alpha$ having the same type as R (theorem 1 of [1]). See also [7].

These results allow to justify easily the following examples.
For the free energy $F(T, V, N)$, one has $F = U - TS$, thus F is a quasi-homogeneous function of degree 1 and of weights $(0, 1, 1)$, and

$$F(T, V, N) = V\, \frac{\partial F}{\partial V} + N\, \frac{\partial F}{\partial N}. \tag{10}$$

Analogously,

$$S(T,V,N) = V\,\frac{\partial S}{\partial V} + N\,\frac{\partial S}{\partial N}. \tag{11}$$

[In fact, $S = -\partial F/\partial T$ and theorem 1 of [1] can be applied]. Moreover, given $S(T,p,N)$, one has

$$S(T,p,N) = N\,\frac{\partial S}{\partial N}. \tag{12}$$

In concluding this section, we point out that the distinction between degree and weights of thermodynamic variables is somehow artificial, a degree becoming a weight if the thermodynamic variable is changed into an independent variable (e.g., the degree zero of the pressure becomes a weight zero when p is an independent variable).

III. GIBBS-DUHEM EQUATIONS

Herein we take into account the Gibbs-Duhem equations. Cf. also [5]. Let us define

$$R_i \equiv \frac{\partial R}{\partial x^i}; \qquad R_a \equiv \frac{\partial R}{\partial y^a} \tag{13}$$

one has

$$dR = \sum_{a=1}^{k} R_a\, dy^a + \sum_{i=k+1}^{n} R_i\, dx^i. \tag{14}$$

On the other hand, one obtains from (8)

$$dR = \sum_{i=k+1}^{n} R_i\, dx^i + \sum_{i=k+1}^{n} x^i\, dR_i. \tag{15}$$

The GD equation is then

$$\sum_{a=1}^{k} R_a\, dy^a - \sum_{i=k+1}^{n} x^i\, dR_i = 0. \tag{16}$$

This equation is related with the quasy-homogeneity symmetry of the potential. Let us define the Euler operator

$$X \equiv \sum_{i=k+1}^{n} x^i\,\frac{\partial}{\partial x^i}. \tag{17}$$

Let us also define a 1-form

$$\omega_R \equiv \sum_{a=1}^{k} R_a\, dy^a + \sum_{i=k+1}^{n} R_i\, dx^i \tag{18}$$

where R_a are quasi-homogeneous functions of degree one $X\,R_a = R_a$ and the R_i are quasi-homogeneous functions of degree zero $X\,R_i = 0$. Then ω_R is a quasi-homogeneous 1-form of degree one, in the sense that it satisfies $L_X\,\omega_R = \omega_R$, where L_X is the Lie derivative associated with X. One can also define a function

$$R \equiv i_X \omega_R, \tag{19}$$

where i_X is the standard contraction operator. As a consequence, one finds

$$dR = d(i_X \omega_R) = -i_X\, d\omega_R + L_X\,\omega_R = -i_X\, d\omega_R + \omega_R \tag{20}$$

If ω_R is a closed 1-form (and then, exact in the convex thermodynamic domain), then $d\omega_R = 0$ and $dR = \omega_R$, i.e. R is the potential associated with ω_R. Notice also that in the latter case one finds

$$-i_X\ d\omega_R = 0 \tag{21}$$

which corresponds to the Gibbs-Duhem equation. In fact, one has

$$d\omega_R = \sum_{a=1}^{k} dR_a \wedge dy^a + \sum_{i=k+1}^{n} dR_i \wedge dx^i \tag{22}$$

and

$$\begin{aligned} i_X\ d\omega_R &= \sum_{a=1}^{k} (i_X\ dR_a)\ dy^a - \sum_{a=1}^{k} dR_a\ (i_X\ dy^a) \\ &+ \sum_{i=k+1}^{n} (i_X\ dR_i)\ dx^i - \sum_{i=k+1}^{n} dR_i\ (i_X\ dx^i) \\ &= \sum_{a=1}^{k} R_a\ dy^a - \sum_{i=k+1}^{n} x^i\ dR_i = 0, \end{aligned} \tag{23}$$

where $i_X\ dR_a = X\ R_a = R_a$, and $i_X\ dR_i = X\ R_i = 0$.
The converse is also true, i.e., if (21) is satisfied then from (20) follows that ω_R is closed.
The GD equation is then satisfied because of the equality of the mixed second derivatives of R (Schwartz theorem) and because of the quasi-homogeneous symmetry. In fact, by defining $Q_{\alpha\beta}$ the matrix of the second partial derivatives of R, one finds

$$\sum_{i=k+1}^{n} x^i\ dR_i = \sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i\ Q_{ia}\ dy^a + \sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i\ Q_{ij}\ dx^j. \tag{24}$$

Then the Gibbs-Duhem equation (16) is equivalent to

$$\sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i\ Q_{ia}\ dy^a = \sum_{a=1}^{k} R_a\ dy^a \tag{25}$$

$$\sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i\ Q_{ij}\ dx^j = 0. \tag{26}$$

The former formula (25) is implemented if both Schwartz theorem and the quasi-homogeneous symmetry are implemented. In fact,

$$\begin{aligned} \sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i\ Q_{ia}\ dy^a &= \sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i \left(\frac{\partial}{\partial x^i} \frac{\partial}{\partial y^a} R \right) dy^a \\ &= \sum_{a=1}^{k} \frac{\partial}{\partial y^a} \left(\sum_{i=k+1}^{n} x^i\ \frac{\partial}{\partial x^i} R \right) dy^a \\ &= \sum_{a=1}^{k} \frac{\partial R}{\partial y^a}\ dy^a = \sum_{a=1}^{k} R_a\ dy^a. \end{aligned} \tag{27}$$

Also (26) is implemented, in fact

$$\sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i\ Q_{ij}\ dx^j = \sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i \left(\frac{\partial}{\partial x^i} \frac{\partial}{\partial x^j} R \right) dx^j \tag{28}$$

$$= \sum_{j=k+1}^{n} \left(\sum_{i=k+1}^{n} x^i\ \frac{\partial}{\partial x^i} \frac{\partial R}{\partial x^j} \right) dx^j, \tag{29}$$

and the latter is zero because $\partial R / \partial x^i$ are functions of degree zero for all $i = k+1, \ldots, n$.

IV. PFAFFIAN FORM δQ_{rev}

Let us consider the Pfaffian form δQ_{rev} for a system described by (T, V, N), where T is the absolute temperature; one has

$$\delta Q_{rev} = C_{VN}(T)dT + a(T, V, N)dV + b(T, V, N)dN. \tag{30}$$

δQ_{rev} has to be integrable, i.e., it satisfies $\delta Q_{rev} \wedge d(\delta Q_{rev}) = 0$, and it is known that T is an integrating factor for δQ_{rev}, with

$$\frac{\delta Q_{rev}}{T} = dS. \tag{31}$$

Then, one finds that

$$\frac{\delta Q_{rev}}{T} = \frac{C_{VN}(T)}{T}dT + \frac{a(T, V, N)}{T}dV + \frac{b(T, V, N)}{T}dN \tag{32}$$

is exact and a potential is given by

$$S = \frac{a(T, V, N)}{T}\, V + \frac{b(T, V, N)}{T}\, N. \tag{33}$$

Notice that the quasi-homogeneity of degree one of S is the tool allowing to obtain this result. It is "trivial" that S is the potential associated with $\delta Q_{rev}/T$, it is less trivial that its "homogeneity" leads to (33). For a proof, see the appendix. δQ_{rev} is quasi-homogeneous of degree one and weights $(0, 1, 1)$. From the theory of quasi-homogeneous integrable Pfaffian forms [7], it is known that an integrating factor is also given by

$$f = a(T, V, N)\; V + b(T, V, N)\; N. \tag{34}$$

The proof is found in Ref. [7]. It is evident that

$$f = TS. \tag{35}$$

Analogously, one can consider (T, p, N) as independent variables

$$\delta Q_{rev} = C_{pN}(T)dT + \eta(T, p, N)dp + \zeta(T, p, N)dN, \tag{36}$$

in which case

$$f = \zeta(T, p)\; N = TS. \tag{37}$$

APPENDIX A: POTENTIALS OF EXACT QUASI-HOMOGENEOUS PFAFFIAN FORMS

We show that, if

$$\omega = \sum_{a=1}^{k} B_a(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n)\; dy^a + \sum_{i=k+1}^{n} B_i(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n)\; dx^i \tag{A1}$$

is a C^2 exact quasi-homogeneous Pfaffian form of degree one, with B_a, x^i quasi-homogeneous of degree one and B_i, y^a quasi-homogeneous of degree zero with respect to the Euler operator

$$Y = \sum_{i=k+1}^{n} x^i \frac{\partial}{\partial x^i}, \tag{A2}$$

then

$$P(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \equiv \sum_{i=k+1}^{n} B_i(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n)\; x^i \tag{A3}$$

is a potential associated with ω. In fact, let us consider

$$dP = \sum_{i=k+1}^{n} B_i(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dx^i + \sum_{i=k+1}^{n} x^i\,dB_i(y^1,\ldots,y^k,x^{k+1},\ldots,x^n) \tag{A4}$$

$$= \sum_{i=k+1}^{n} B_i(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dx^i + \sum_{i=k+1}^{n} x^i \sum_{j=k+1}^{n} \frac{\partial B_i}{\partial x^j}(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dx^j \tag{A5}$$

$$+ \sum_{i=k+1}^{n} x^i \sum_{a=1}^{k} \frac{\partial B_i}{\partial y^a}(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dy^a. \tag{A6}$$

The exactness of the Pfaffian form ω implies that $d\omega = 0$ and, in particular

$$\frac{\partial B_i}{\partial y^a} = \frac{\partial B_a}{\partial x^i} \qquad a = 1,\ldots,k;\ i = k+1,\ldots,n, \tag{A7}$$

$$\frac{\partial B_i}{\partial x^j} = \frac{\partial B_j}{\partial x^i} \qquad i,j = k+1,\ldots,n \tag{A8}$$

Then, one obtains

$$\sum_{i=k+1}^{n} x^i \sum_{a=1}^{k} \frac{\partial B_i}{\partial y^a}(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dy^a = \sum_{i=k+1}^{n} x^i \sum_{a=1}^{k} \frac{\partial B_a}{\partial x^i}(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dy^a \tag{A9}$$

$$= \sum_{a=1}^{k} \left(\sum_{i=k+1}^{n} x^i \frac{\partial}{\partial x^i} B_a(y^1,\ldots,y^k,x^{k+1},\ldots,x^n) \right) dy^a \tag{A10}$$

$$= \sum_{j=1}^{k} B_a(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dy^a, \tag{A11}$$

because each B_a is quasi-homogeneous of degree one. On the other hand, one has

$$\sum_{i=k+1}^{n} x^i \sum_{j=k+1}^{n} \frac{\partial B_i}{\partial x^j}(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dx^j = \sum_{i=k+1}^{n} x^i \sum_{j=k+1}^{n} \frac{\partial B_j}{\partial x^i}(y^1,\ldots,y^k,x^{k+1},\ldots,x^n)\,dx^j \tag{A12}$$

$$= \sum_{j=k+1}^{n} \left(\sum_{i=k+1}^{n} x^i \frac{\partial}{\partial x^i} B_j(y^1,\ldots,y^k,x^{k+1},\ldots,x^n) \right) dx^j \tag{A13}$$

$$= 0, \tag{A14}$$

because each B_i is quasi-homogeneous of degree zero.

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